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Green Chemistry Conception in Redox Polymers Synthesis

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Abstract

Various approaches have been considered in respect of the synthesis of redox polymers: polycondensation of active redox monomers, chemical modification of inert macromolecules by quinones, and polymerization of nonsaturated monomers in conditions of cationic and radical initiation. Both advantages and disadvantages have been discussed from the point of view of green chemistry. Sorption and redox properties of synthesized redoxites have been identified.

1. Introduction

Rapid development of polymer chemistry in the early 1920s and 1930s provided the humankind with such various useful materials, as: medications, perfumery products, construction materials, etc. However, there is a flip side of this successful process: along with the intensification of chemical industry research, all of air, water and soil are being contaminated by industrial waste in the form of toxic gas, waste mud and chemical synthesis byproducts.

The lack of attention to environmental protection issues, poor control by the state, and legal nihilism on the part of people have all triggered serious environmental consequences and hard conditions for human life. “Infected and polluted water, destroyed fertile soil, vast extermination of forests, extinction of a majority of species of valuable animals, and spoiled ambient air – this is the result of the environmental policy, or most likely the absence of such policy” [1]. Such problems arise everywhere in the world, because the environment is the last thing on which the state, and especially private entrepreneurs, spends their money.

Thus, air, ground water, surface water, and soil become environmentally hazardous to a human. This is particularly evident where industrial and agricultural projects are being implemented. The deterioration of water quality and the enhanced standards for drinking water require improved methods of water treatment. Depending on the degree of pollution, various treatment methods are used, of which the most widespread are an ion exchange method [2-4]. Along with ion exchange resins, the most promising are redox resins or redox polymers [5-7]. Due to the presence of ionic or electro-exchange groups, such polymers act in a dual mode: they are involved in reversible redox reactions and in ion exchange or complex forming. This will allow using them to extract precious, rare and dispersed elements, and heavy metals [8-13]. Furthermore, they are potentially capable to regeneration and multiple use, which to certain extent may compensate for initial production costs. This makes them a promising class of high-molecular compounds.

2. Experimental

2.1. Synthesis of Redox Polymers

Synthesis of redox polymers (RP) on the base of polystyrene or copolymers of styrene with DVB and quinones - 1,2- and 1,4-Quinones (Q), 1,2- and 1,4-Naphthoquinones (NQ), anthraquinone (AQ) - was carried out by their condensation in the medium of freshly distillated solvents at the temperature of 7-100ºC during 1-8 hrs in the presence of Fridel-Crafts catalysts ($AlCl_3$, $ZnCl_2$ or $SnCl_4$) [14]. Copolymers were washed off from unreacted components by decantation, then by methyl (ethyl) alcohol in Sohxlet apparatus.

2.2. Oxidation-Reduction Potentiometric Measurment

The redox capacity of reduced samples was determined in the argon atmosphere under 0,1N solution of $Fe_2(SO_4)_3$. Oxidized-reduced potentiometric titration of the reduced polymers was carried out on a titrometer of the firm Mettler-Toledo in a thermostated cell in the argon flow by solution of $Ce(SO_4)_2$ in sulfuric acid, standartized with 0.1N solution of $Na_2S_2O_3$ in the presence of a calomel electrode with a smooth platinum electrode at the temperature of 25ºC. As mediator in the case of cross-linked redox-polymers, 1/30N solution of Fe^{3+} in a buffer of K_2SO_4+H_2SO_4 at pH 0.6-0.7 was used [5].

2.3. The Synthesis of Aminoquinoid Redox Polymers

The synthesis of redox polymers based on polyamines (PA) and quinones (Q) was carried out in various solvents at various mole ratios of initial PA:Q reactants, and at various temperature and time modes [12, 13, 15]. The pH level was adjusted by adding ammonia, sodium hydroxide or sodium acetate. As soon as the reaction terminated, the polymer was separated, purified with methyl (ethyl) alcohol in a Soxhlet extractor, treated by 4% NaOH, washed until the wash water showed neutral reaction, where after the key physical and chemical properties were identified.

2,3,5,6-tetrachlorbenzoquinone (TClBQ) or chloranil (ChA); 2,3-dichlor-5,6-dihydroxybenzoquinone (DClDHBQ) or chloranillic acid (ChAAc); 2,3-dichlornaphtoquinone (DClNQ) were used as chlorine containing quinones.

2.4. Measurement of Physical-Chemical Characteristics

The progress of the reaction was assessed in view of the data obtained by way of elemental analysis and IR spectroscopy, as well as by referring to redox capacity (RC) and static exchange capacity (SEC) upon the main groups of final products, and the values of potentiometric acid-base and redox titration measured [5] by DL50 titration apparatus Mettler Toledo at 25^0. IR-spectra of samples were taken on a spectrophotometer “Specord M-80/M-85 in tablets with KBr (200 mg of KBr + 1 mg of substances).

2.5 The Synthesis Quinoid Derivatives of Allylamine and Monoethanolamine Vinyl Ether

The synthesis of AA (allylamine) and VEMEA (vinyl ether monoethanolamine) derivatives of quinones, involving high output, was carried out at a room temperature in organic or water-organic medium [16, 17]. Homopolymerization and copolymerization of mono- and disubstituted redox monomers based on various quinones were carried out in conditions of cationic and radical initiation [9,11].

2.6. The Oxidizing Ability of Redox-Polymers

The oxidizing ability of redox-polymers was assessed on the basis of the yield of organic phosphorus compounds (OPCs) generated in terms of oxidation of phosphine. The experimental procedure is described in publications [18]. Obtained OPC identified GL chromatography methods, $NMR^{31}P$-, IR-spectroscopy, and also at temperatures of boiling and refraction indicators. IR-spectra obtained OPC registered on the Specord M80/M85, spectra $ЯМР^{31}P$ - on "Bruker" AHM-400 and WP-80 spectrometer in relation to 75 % H_3PO_4, indicators of refraction (n_D^{20}) are established on the IRF-454 refractometer.

2.7. Sorption of Ions of Heavy and Scattered Metals

Sorption of ions Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{6+}, Re^{7+} by the redox polymers on the base of PA OH-form was studied under static conditions at the module solution/sorbent of 400, room temperature, 20±2°C and a contact time of 7 days, varying concentration in copper sulphate solution from 0.097 to 1.853, nickel – from 0.112 to 2.158, cobalt – from 0.105 to 2.166, zinc – from 0.119 to 2.109, chromium – from 0.205 to 2.080, renium – from 0.102-1.024 g/l. For the preparation of model solutions $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}7H_2O$, $CoSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $K_2Cr_2O_7$, NH_4ReO_4, salts of qualification "chem. pure" are used.

Sorption capacity (SC) was calculated from the difference between the initial and equilibrium concentration of the solution, which was determined by the method of classical polarography against 0,5 M NH_4Cl on the waves of recovery Cu^{2+} ($E_{1/2}$= 0,16 V), Ni^{2+} ($E_{1/2}$= - 1,07 V), Co^{2+}($E_{1/2}$= -1,07 V), Zn^{2+} ($E_{1/2}$= -1,02 V), $Cr_2O_7^{2-}$ ($E_{1/2}$= - 0.17 V), ReO_4^- ($E_{1/2}$ = - 0,50 V).

Polarography is a valid and reliable physical and chemical methods of analysis, characterized by high sensitivity, rapidity and objectivity of the results. At using a polarographic method error in determining the concentration of metals does not exceed 2-3 rel.%. Polarogram take on a universal polarograph PU-1 in thermostated cell at 25±0,50 °C using a dropping mercury electrode. Oxygen from the test solutions were removed by blowing argon for 5 minutes. Saturated calomel electrode served as the reference electrode.

3. Results and Discussion

However, all of the known methods for producing RP by way of polycondensation or chemical modification in respect of the relevant monomers or polymers involve multiple stages and occur in harsh conditions in aggressive environments. For the majority of such methods, preliminary functionalization of macromolecules is required to be carried out in various stages through nitration by concentrated nitric acid and subsequent recovery of nitric derivatives in autoclave, halogenmethylation, diazotization, etc. [5-7, 15].

In this regard, the green chemistry concept [19-22] that was proposed in the 1990s by P.T.Anastas and J.C.Warner represents a promising way for the environmental protection from chemical and industrial pollution. This concept offers advanced and sophisticated scientific approaches to certain environmental issues.

Unfortunately, very few technologies have been so far created that would meet the green chemistry requirements. While such kinds of research are very popular in both organic and pharmaceutical chemistry, this is not true for polymer chemistry. Meanwhile, polymer chemical products are widely used in daily life.

3.1. Synthesis of Quinoid Polymers on the Base of Copolymers of Styrene and Divinylbenzene

Arylation of quinones, under Friedel–Crafts reactions, represents a promising method, which would exclude any chloromethylation and amination stages, on Hill D. and Adams H. studies [23]. They indicated that interaction of the aromatic compounds with quinones under conditions of Friedel-Crafts reaction leads to the formation of diarylhydroquinones. And quinoid group serves as an acceptor of the part of separating hydrogen as illustrated in fig 1:

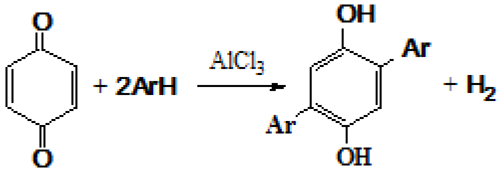

Fig. 1. Interaction of aromatic compounds with quinones under conditions of Friedel-Crafts reaction.

The displacement reaction with formation of monoderivatives does not occur. 2,5-diarylhydroquinones easily transforms into the appropriate diarylquinones at oxidation of Fe^{3+} in acetic acid, chromic acid, and other oxidants, and also excess of quinone itself (fig 2):

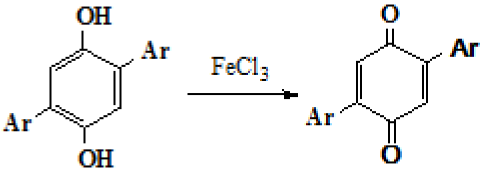

Fig. 2. Oxidation of diarylquinones at different oxidiezers.

Hydrogen sulfide, aromatic compound itself, benzene are used in this reaction as solvents. Chloride aluminum and other catalysts react with quinones forming stable complexes. They are released as far as the process goes.

As an aryl component we used styrene and divinylbenzene copolymers or polystyrene [14] (fig 3):

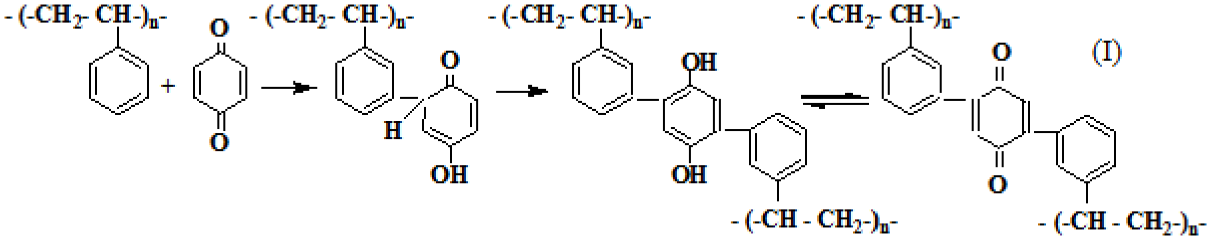

Fig. 3. Interaction of polyvinylaromatic compounds with quinone under conditions of Friedel-Crafts reaction.

However, RP so formed are hydrophobic and, therefore, show insufficiently high redox capacity. In order to optimize the functions of such polymers, hydrophilization of the product of reaction is required. Thus, the number of stages increases. Furthermore, stoichiometric ratios of the components would be required. The presence of an equimolar amount of the catalyst, which requires to be utilized, results in the aggravation of the situation. It is known that in green chemistry it is advisable to abandon any outdated "stoichiometric" technologies, i.e. one should seek for a solution to the problem by replacing the classic stoichiometric methods with cleaner catalytic methods.

3.2. Synthesis of Quinoid Polymers on the Base of Polyamines

A successful solution would be to use aliphatic PA (such as PEI or PEPA), which are universally well produced. The latter constitute the simplest heterochain polymers and polybases. They are formed by replacing one thirds of carbon atoms in polyethylene with nitrogen atoms. While retaining certain properties of polyethylene (including thermstability), they acquire a high reaction ability. Due to the positive induction influence of hydrogen atoms in $-CH_2-CH-$ on primary amino-groups PA, they are outstanding in their high electronegativity, which results in high reaction ability in substitution reactions. In addition, low molecular mass of the inert polymer matrix, as applicable to aliphatic polyamines, allows obtaining sorbents with high rates of exchange, sorption and redox capacity [12,13, 24].

The synthesis of redoxionites based on aliphatic polyamines and quinones was carried out by: a reaction of reductive joining of quinones to amines (I) and a reaction of nucleophilic substitution of a halogen in chlorine quinones (II). In the first case (I) the interaction between quinones and amines occurs in the same manner as with unsaturated open chain α, β-diketones through the stage of reductive joining of quinones to polyamines. At an intermediate stage, a quinoid system is transformed into an aromatic system. At this stage, as a result of enolization of the addition product (1), substituted hydroquinones are formed (2). They are oxidized in the excess of a quinone to substituted quinone (3), which them is capable of reattaching an amine obtaining a disubstituted derivative (4) [25] as illustrated in fig 4:

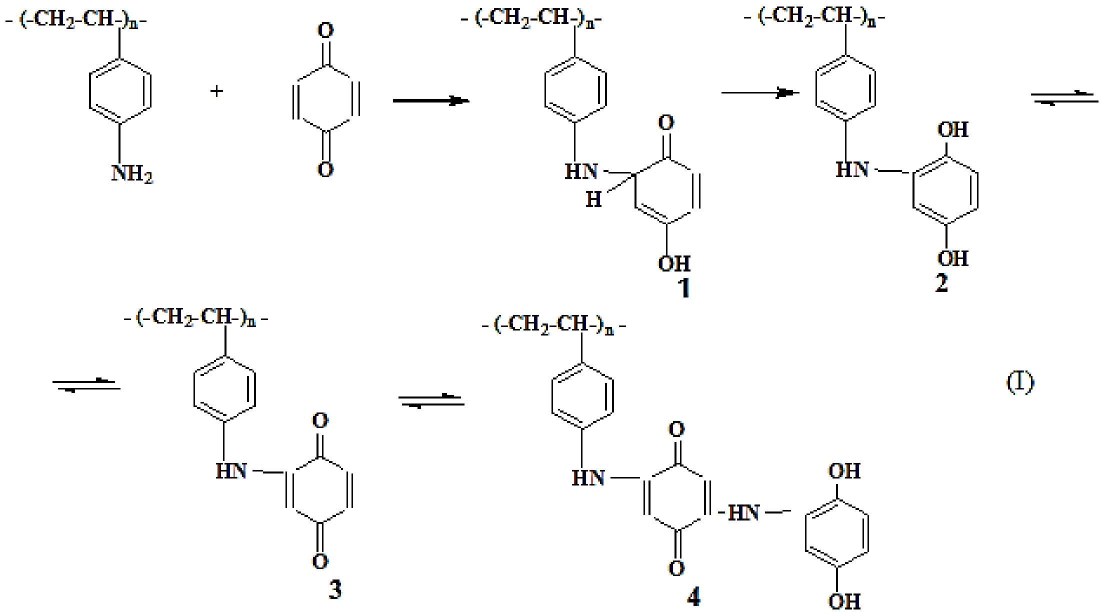

Fig. 4. A reaction of reductive joining of quinones to polyamines.

When aminopolymers interact with chlorine quinones, the reaction proceeds under the conditions of nucleophilic substitution of a halogen by compounds, which are capable to make reversible redox reactions (quinones, di- and trioxybenzenes and their derivatives) (II) [15, 25] (fig 5):

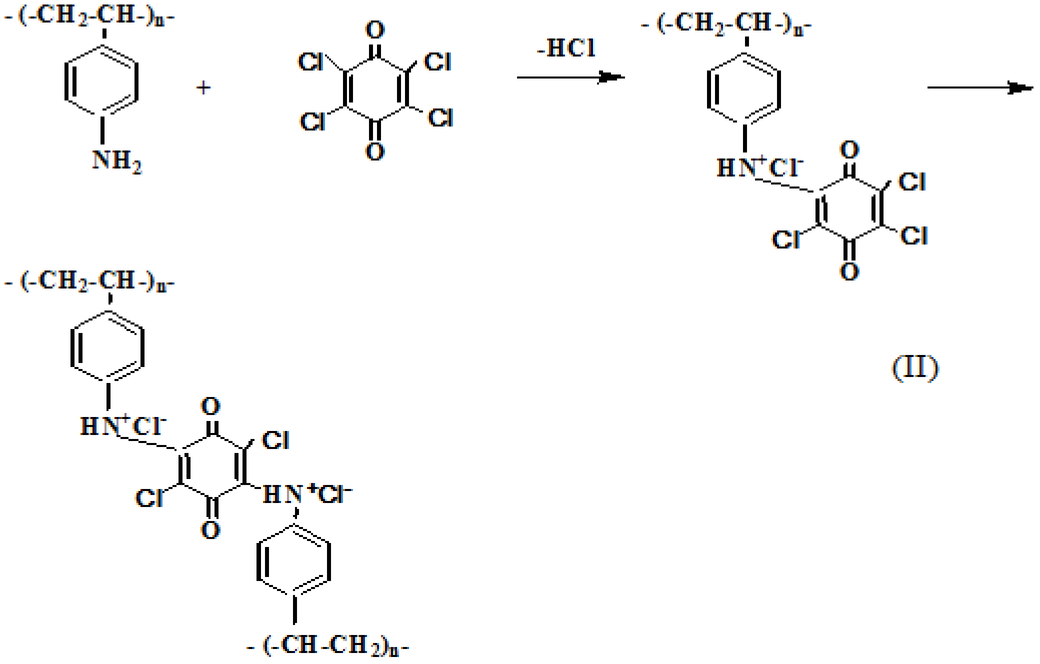

Fig. 5. Formation of polyaminoquinones on reaction of nucleophilic substitution of chlorine in the chloroquinones

Monosubstituted derivatives are formed at the first stage, and disubstituted derivatives are formed at the second stage causing further joining in the polymer chain. Hydrogen halogen formed at the first stage is involved in salt formation; at the second stage of the reaction, ammonium salt is destroyed under the impact of free amino groups of the polymer that act as a base.

3.3. Synthesis of Quinoid Polymers on the Base of Unsaturated Derivatives of Quinones

Few stages of and highly effective methods for obtaining redox polymers can be implemented by polymerization of unsaturated derivatives of quinones. However, vinyl quinone derivatives are unknown, and vinylhydroquinones are formed through multiple stages of "blocking the groups, introducing and releasing protection" [5,6]. Therefore, the idea of using glycerol and carbide byproducts, as "double bond carriers", such as allylamine (1) and vinyl ester monoethanolamine (2), has occurred. That idea has been successfully realized for the synthesis of aminoquinoid redox polymers [9]. The initial presence of a primary amino group in those compounds excludes any stage of ascribing functions to a monomer that is usually required for further chemical transformations. The synthesis of AA and VEMEA quinoid derivatives with high yields is carried out at room temperature in organic or water-organic medium [16,17].There are formed mono- and disubstituted redox monomers based on various quinones as illustrated in fig 6:

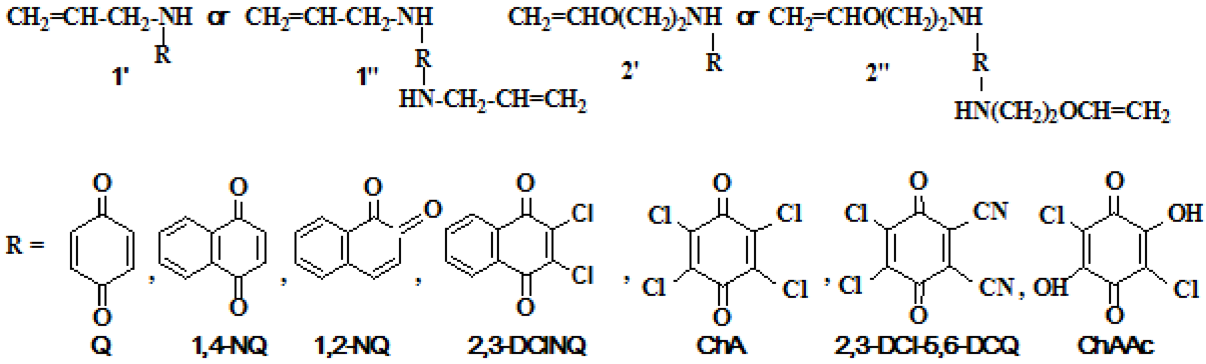

Fig. 6. *Structure of mono- (1', 2') and disubstituted (1'', 2'') quinoid derivatives of AA (1', 1'') and VEMEA (2', 2'').*

As might have been expected, the modification of AA and VEMEA by such strong electron acceptors as quinones essentially increases the reactivity of double bonds of these monomers, which are hard to subject to polymerization and often almost non susceptible to polymerizations. When quinones are added, the electron density changes its order and the π-electron cloud is displaced towards an electron-accept substituent. Such a displacement is accompanied by a decrease in the degree of mutual overlapping of π-electron clouds towards the double bond, an increase in energy costs for disclosure of double bonds between VEMEA and AA and for their polarization. As a result, the reactivity of a polymer radical is enhanced and the quinoid derivatives are quite easily involved in polymerization.

3.4. Study of Kinetic Polymerization of Unsaturated Derivatives of Quinones, AA and VEMEA

Our research confirms the aforesaid. We found [9] that synthesized unsaturated derivatives of quinones enter easily into homo- and copolymerization reactions, and they are successfully polymerized in the presence of both radical catalysts and cationic catalysts, as is evidenced by the energy of activation of homopolymerization of quinoid redox monomers based on AA and VEMEA and by the yields of final products (Table 1) [26].

Table 1. *E_{act} of polymerization of quinoid derivatives of AA and VEMEA and yield of redox polymers*

Redox monomer	E_{act}, kJ.Mol^{-1}/ Yield, %	
	Radical polymerization	Cationic polymerization
VEMEA-Q	76,71/49,3	28,80/57,7
VEMEA-Q-VEMEA	11,95/67,8	42,40/96,0
VEMEA-1,2-NQ	62,50/52,9	-
VEMEA-1,4-NQ	82,84/55,9	50,70/51,4
VEMEA-ChA	50,43/54,0	-
VEMEA-ChA-VEMEA	110,35/28	14,42 /96,0
VEMEA-2,3-DCl-5,6-DCQ	47,34/61,0	63,75/83,0
VEMEA-2,3-DCl-1,4-NQ	69,40/32,5	63,32/94,0
AA-Q	47,24/59,0	-8,41
AA-Q-AA	66,23/58,0	-19,10
AA-1,2-NQ	-	8,65/96,0
AA-ChAAc	-	33,19
AA-2,3-DCl-5,6-DCQ	-	14,92

*Q – Quinone, NQ – Napthoquinone, ChA - Chloroanyle, DClDCQ – 2,3-dichloro-5,6– dicyanoquinone, ChAAc – chloroanylic acid

As can be seen, depending on the nature of a quinone, the energy of activation takes different values, which are lower in conditions of cationic initiation. Exceptions include VEMEA-Q-VEMEA and VEMEA-DCDCQ monomers. This data requires further interpretation. Usually E_{act} of cationic polymerization varies from -10 to +15 kcal/mol (from -42 to +63 kJ/mol) [27]. The values of activation energy that we have found are within these rates.

Because of lower energy costs for cationic polymerization of the aforesaid monomers, the synthesis redox polymers in question is preferred. It allows complying with many of twelve positions of Green Chemistry, which were formulated by the authors of the first monograph [19] and which should be relied on by researchers. Importantly, the synthesis of redoxionites by polymerization of the aforesaid monomers in terms of cationic initiation takes place at room temperature and atmospheric pressure, without any emission of harmful byproducts, in the presence of few catalysts with high yields, and the final products are nontoxic. As the reaction is carried out only at one stage, energy is saved further, thus improving both environmental and commercial assessment of the synthesis. The lack of byproducts, which would require disposal, eliminates any difficult stages of destruction or recycling. However, in order to improve the process described a lot of things would need to be done, such as: replace organic solvents by “green” solvents, replace corrosion hazardous catalysts by those, which would be less aggressive but equally effective, etc.

Quinoid redox polymers were tested as oxidants [18, 28] and sorbents [10, 12, 13,24, 29-31].

3.5. Study the Oxidation Ability of Synthesized Redox Polymers

Oxidation properties of redox polymers was surveyed by examining the oxidation of phosphine towards organic phosphorus acids (Table 2).

Table 2. *Oxidation of phosphine in alcohol solutions of a RP based on PA and 2,3-DClNQ**

N	I_2,mmol - RP	BuOH, ml	$PH_3 \cdot 10^{-3}$, Pa	$(RO)_2HPO$, %	$(RO)_3PO$,%
1	RP	2,0	1,0	-	-
2	0,1-RP	2,0	1,0	17	7
3	0,2- RP	6,0	1,3	10	52
4	0,2-RP	8,0	1,3	21	42
5	0,2-RP	10,0	1,7	49	51
6	0,7-RP	10,0	1,7	40	60
7	1,5- RP	10,0	1,7	30	70

*50^{0}C, 2 g, solvent DMFA

The synthesis of phosphoric acid esters from phosphoric hydrogen PH_3 and aliphatic alcohols is based on the oxidation of phosphine by quinones and redox polymers on the basis of PA. Molecular iodine is used as a catalyst. Two-, three-, four- and multicomponent systems are studied in order to determine optimal conditions of the oxidation of phosphine quinones and repoxpolymers on their basis. The rate and selectivity of reaction were monitored by the absorption of PH_3. As alcohols used aliphatic alcohols: BuOH, PrOH, EtOH, MeOH.

Organophosphorus compounds were analyzed by a chromatographic method. It was established that alcohol solutions of individual components of reactionary system (quinones, redox ionites or iodine) are characterized by a low activity in relation to phosphine (Exp.1,2). Organophosphorus compounds are formed in insignificant quantities. In the mixed alcohol solution of benzoquinone takes place PH_3 oxidation forming trialkylphosphates. Conversion of phosphine constitutes 80-100%. Increasing the concentration of reagents of catalytic system has a positive effect on the process as a whole. Similar patterns were obtained when redox monomers and polymers on the base of quinones in the presence of iodine were used as oxidants. Esters of phosphoric acid – dialkylphosphites and esters of phosphorous acid – trialkylphosphates were identified as organophosphorus compounds (Exp.2-7).

By selecting a redox agent in a zone of the catalysis it is possible to direct process in the desirable direction. Results of our experiments and literature data on oxidation-reduction processes with participation of iodine and quinones in organic solutions allowed to propose the separate oxidation-reduction mechanism of formation of organophosphorus compounds. In investigated multicomponent systems, the synergetic effect is manifested which is reached at the expense of distribution of oxidation-reduction functions among iodine, quinones and its derivatives. It is established reactionary ability of quinones and redox ionites on their basis in an oxidizing alkoxylation of phosphine to valuable esters of acids of phosphorus. Reaction can be used for purification of exhaust and technological gases from phosphine and its utilization.

3.6. Study the Sorption Ability of Synthesized Redox Polymers

The data relating to polarographic survey of the sorption activity in synthesized redox polymers as compared with ions of various metals is shown in Table 3.

Table 3. *Performance of the sorption of redox polymers based on PA and quinones per certain metal ions*

Metal RP	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cr^{6+}	Re^{7+}
PEI-CA	466,0	355,2	194,4	104.4	416,0	368,4
VEMEA-CA	254,2	220,1	287,6	-	-	-
AV-17 [29]	-	-	-	60,1	231,6	-
AMP[30]	111,2	103,0	121,3	-	240,4	-
AN-21	-	-	-	-	-	343,0

Because the structure of redox polymers based on PA and quinones contains the -NH-, =N-, >C=O groups, which in turn contain nitrogen and oxygen atoms with unshared pairs of electrons, polymers are able to form complexes. Ions of transition metals with free valence orbits may form chelate coordination compounds, due to donor-acceptor interaction.

As can be seen, synthesized redox polymers have a higher sorption capacity than commercial samples. In certain cases, the samples differ in their selective properties. For example, a selective extraction of Cu^{2+} and Zn^{2+} ions is observed in the presence of Ni^{2+} and Co^{2+} ions. This can be used in analytical chemistry.

4. Conclusion

Thus, the analysis of various methods for the synthesis of redox polymers shows that there are different approaches to obtain them. Importantly, following the green chemistry concept, a desired substance should be obtained in such a way that no harm is caused to the environment at any stage of the synthesis, and that the process is both commercially viable and environmentally acceptable.

Abbreviations

AA	Allylamine
AQ	Anthraquinone
BuOH	Butyl alcohol
DMFA	Dimethylformamide
DVB	Divinylbenzene
DClDHBQ, or ChAAc	2,3-Dichlor-5,6-dihydroxybenzoquinone, or chloranillic acid
DClNQ	2,3-Dichlornaphtoquinone
EtOH	Ethyl alcohol
MeOH	Methyl alcohol
VEMEA	Vinyl ether monoethanolamine
NPhQ	1,2- and 1,4-Naphthoquinones
OPCs	organic phosphorus compounds
ORC	Oxidation-reduction capacity, mg-equ/g
PA	Polyamine
PEI	Polyetheleneimine
PEPA	Polyethylenepolyamine
PrOH	Propyl alcohol
Q	Qunone
RP	Redox polymer
RC	Redox capacity, mg-equ/g
SEC	Static exchange capacity, mg-equ/g
SC	Sorption capacity, mg-equ/g
TChBQ, or ChA	2,3,5,6-Tetrachloro-p-benzoquinone, or Chloroanyl
AV-17	Industrial strong-basic anion exchanger
AMP	Industrial strong-basic anion exchanger
AN-21	Industrial weak-basic anion exchanger

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